

# Low Temperature Symmetry of Pyrochlore Oxide $\text{Cd}_2\text{Re}_2\text{O}_7$

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We report the X-ray study for the pyrochlore oxide  $\text{Cd}_2\text{Re}_2\text{O}_7$ . Two symmetry-lowering structural transitions were observed at  $T_{s1}=200$  K and  $T_{s2}=120$  K. The former is of the second order from the ideal cubic pyrochlore structure with space group  $Fd\bar{3}m$  to a tetragonally distorted structure with  $I\bar{4}m2$ , while the latter is of the first order likely to another tetragonal space group  $I4_122$ . We discuss the feature of the lattice deformation.

A series of pyrochlore oxides  $\text{A}_2\text{B}_2\text{O}_7$  show a variety of interesting conductive and magnetic properties, depending on the substitutions of A and B sites [1]. Geometrical frustration on the pyrochlore lattice leads to an exotic ground state such as spin ice for magnetic insulators [2], while for metallic systems a unique heavy carrier behavior is found in spinel  $\text{LiV}_2\text{O}_4$  having a pyrochlore lattice made of V atoms [3]. In the pyrochlore structure, the A site occupied by a rare-earth or a post-transition metal cation forms a distorted (6+2) coordination, while the B site occupied by a transition metal cation forms a distorted octahedron  $\text{BO}_6$  with an equal B-O distance. The structure comprises two interpenetrating pyrochlore lattices composed of the A or B sites (see Fig. 1).

Recently, Hanawa *et al.* and the others reported the first superconductor  $\text{Cd}_2\text{Re}_2\text{O}_7$  ( $T_c=1$  K) in the family of pyrochlore oxides [4, 5, 6]. The compound exhibits two more phase transitions at  $T_{s1}=200$  K and  $T_{s2}=120$  K, where electrical and magnetic properties change dramatically [7, 8, 9]. The former is of the second order, while the latter is of the first order. These transitions are accompanied by structural transitions. Three phases appearing are named as phase I ( $T>T_{s1}$ ), II ( $T_{s1}>T>T_{s2}$ ), and III ( $T<T_{s2}$ ). Phase I crystallizes in the ideal pyrochlore structure at room temperature with space group  $Fd\bar{3}m$ . It was reported in the recent structure study that the crystal system is still cubic within the experimental resolution in the wide temperature range down to  $T=10$  K [8]. Moreover, taking into account the extinction rule of reflections observed below  $T_{s1}$  in the single crystal XRD experiments, a possible cubic space group of  $F\bar{4}3m$  was suggested. However, recent Re nuclear quadrupole resonance (NQR) experiments have indicated a lack of a threefold axis below  $T_{s1}$  implying that the true symmetry is lower than cubic [10]. In addition, very recent high-resolution XRD measurements using single crystal barely detected a small splitting of cubic Bragg peaks below  $T_{s1}$ , probably due to tetragonal deformation [11]. In this letter, we report the structural study on the low temperature phases of  $\text{Cd}_2\text{Re}_2\text{O}_7$  by means of X-ray diffraction and discuss possible space groups for them.

A single crystal was synthesized as described in the previous paper [4]. We took oscillation photographs using an imaging plate type Weissenberg camera (Mac Sci-

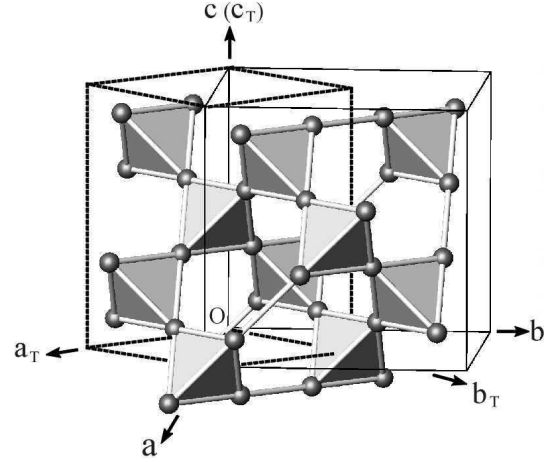


FIG. 1: Pyrochlore lattice on Re (=B site) atoms with cubic and tetragonal cell shown. A body-centered tetragonal lattice made by the transformation  $\mathbf{a}_T=(\mathbf{a}-\mathbf{b})/2$ ,  $\mathbf{b}_T=(\mathbf{a}+\mathbf{b})/2$  and  $\mathbf{c}_T=\mathbf{c}$  is illustrated by the dashed line.

ence DIP320V) equipped with a closed-cycle helium refrigerator, which is a specialized system with very low background, in the temperature range of 10 K–300 K. The intensity data was collected by a four-circle diffractometer (Mac Science MXC) using a  $2\theta-\omega$  scan mode and a CCD area detector (Bruker SMART APEX) equipped with a helium flow type cooler in the temperature range of 85 K–300 K. These measurements were performed using a 21 kW rotating-anode X-ray generator with a graphite monochromated Mo- $K\alpha$  radiation. The cooling or heating rate was fixed to 0.5 K/min around the first-order transition at  $T_{s2}$ .

First, we carefully took oscillation photographs in the whole temperature range. Neither additional reflection breaking the face-centered lattice nor peak splitting of reflections were observed. However, the forbidden reflections were found below  $T_{s1}=200$  K. Figure 2 (a) shows the temperature dependence of peak intensity for two types of reflections ( $0kl : k+l\neq 4n$ ,  $00l : l\neq 4n$ ), which are extinguished in  $Fd\bar{3}m$ . They increase gradually below  $T_{s1}$  with decreasing temperature, indicating that the transition is of the second order. Moreover, the slight anomaly was observed for some reflections at  $T_{s2}=120$  K.

FIG. 3: Group-subgroup relations of symmetry reductions for the maximum subgroups, using the conventional space group setting. Symmetry reductions from face-centered to body-centered lattice are described by the translational-equivalent of index 3 ( $t3$ ) with the cell transformation, and the other reductions are described by  $t2$ .

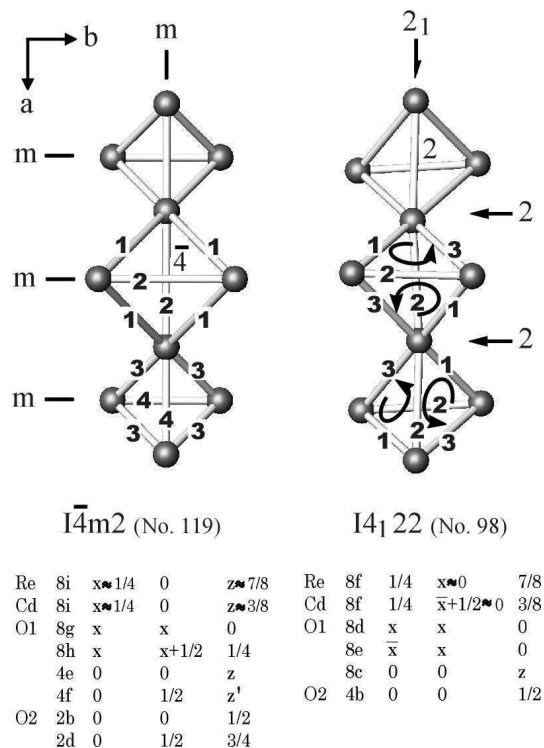


FIG. 4: Schematic representations of Re tetrahedra and atom positions for  $I\bar{4}m2$  (left) and  $I4_122$  (right). Deformation of Re tetrahedra expected for each space group is illustrated exaggeratedly. Numbers on the bonds for  $I\bar{4}m2$  and  $I4_122$  correspond to four and three kinds of bond lengths, respectively. Rotational arrows imply a possible *bondchirality* pattern. Parameter  $x, z (\approx x_0 - 1/8)$  and  $z' (\approx x_0 + 1/8)$  on O1 atom is related to the distortion of the  $\text{ReO}_6$  octahedron. The value of  $x_0 = 0.3186(6)$  is estimated from our structural data at 300 K, which is different from  $x_0 = 0.3089(7)$  in Ref. 7.

Next, we discuss the symmetry of phase III. We checked all the body-centered tetragonal lattices, and found that only the space groups shown in Fig. 3 could construct the pyrochlore structure. Since the transition at  $T_{s2}$  is of the first order, the space group at phase III seems not to be included in the subgroup of  $I\bar{4}m2$ . Therefore, possible space groups are  $I4_1/amd$ ,  $I\bar{4}2d$ ,  $I4_1/a$ ,  $I4_122$ ,  $I4_1md$  and  $I4_1$ . Here, we can exclude  $I4_1/amd$ ,  $I\bar{4}2d$ ,  $I4_1/a$  and  $I4_1md$ , because these are not compatible with the observed extinction condition of reflections with considering a possible crystal twinning. On the other hand, there is no way to distinguish a true one among the other two space groups of  $I4_122$  and  $I4_1$  from our experiments. However, the CBED experiments suggested that the point group of phase III is  $422$  [13]. This fact makes one space group  $I4_122$  selected unambiguously. Thus, it is plausible that a symmetry change from  $I\bar{4}m2$  to  $I4_122$  occurs at  $T_{s2}$ , which means missing a mirror symmetry and adding a twofold axis. Such an exchange in symmetry operations is generally seen in a first-order phase transition. It is interesting to note that the Re

atom coordinate changes from  $(x \approx 1/4, 0, z \approx 7/8)$  in  $I\bar{4}m2$  to  $(1/4, x \approx 0, 7/8)$  in  $I4_122$ . Then, in the  $I4_122$  structure, the three kinds of Re-Re bond lengths exist, and the each volume of Re tetrahedron is equivalent. Let's call the three bonds as 1, 2 and 3 in order of bond length. When we trace the bonds of each tetrahedral face as  $1 \rightarrow 2 \rightarrow 3$ , as shown in Fig. 4, a left-rotation (counter-clockwise) configuration can be defined. Then, all the tetrahedral faces possess the same left-rotation configuration. It is naturally expected that a right-rotation configuration is also realized with equal probability. We call this topological chirality on the Re tetrahedra "*bondchirality*" by analogy with the *R-S* convention for a chiral molecule in organic chemistry. The direction of rotation depends on the sign of the Re atom parameter. In a real crystal, two types of domain with the left and right rotations are formed below  $T_{s2}$  as a racemic mixture. The Re tetrahedron in  $I\bar{4}m2$  is considered to be a disordered state without *bondchirality*. This means that the transition at  $T_{s2}$  is relevant to ordering of the *bondchirality*.

In summary, we have reported the low temperature X-ray study for the first pyrochlore oxide superconductor  $\text{Cd}_2\text{Re}_2\text{O}_7$ . The breaking of the cubic lattice and inversion symmetry are observed below  $T_{s1} = 200$  K as well as below  $T_{s2} = 120$  K. From the experimental findings and the group-subgroup relations, it is suggested that the space group changes from  $Fd\bar{3}m$  to  $I\bar{4}m2$  at  $T_{s1}$ , and to  $I4_122$  at  $T_{s2}$ . In addition, the characteristic deformations of Re tetrahedron were discussed in each phase.

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